New Theoretical Approach to Quantum Size Effects of Interactive Electron-hole in Spherical Semiconductor Quantum Dots

B. Billaud* and M. Picco

Laboratoire de Physique Théorique et Hautes Energies (LPTHE),
CNRS UMR 7589, Université Pierre et Marie Curie (Paris VI),
4, place Jussieu, 75252 Paris Cedex 05, France.

T.-T. Truong

Laboratoire de Physique Théorique et Modélisation (LPTM),
CNRS UMR 8089, Université de Cergy-Pontoise,
2, avenue Adolphe Chauvin, 95302 Cergy-Pontoise Cedex, France.

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Abstract

The issue of quantum size effects of interactive electron-hole systems in spherical semiconductor quantum dots is put to question. A sharper theoretical approach is suggested based on a new pseudo-potential method. In this new setting, analytical computations can be performed in most intermediate steps lending stronger support to the adopted physical assumptions. The resulting numerical values for physical quantities are found to be much closer to the experimental values than those existing so far in the literature.

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*Also at LPTM, Université de Cergy-Pontoise; Electronic address: baptiste.billaud@u-cergy.fr

I. INTRODUCTION

For about three decades, nanostructures — produced by many techniques such as etching, local inter-diffusion, particle suspension in dielectric media, or by self-assembly in matrices of a host material — are known as confined electronic systems because they are designed to restrict particle motion to a space region with a restricted number of dimensions. Depending on their dimensionality, these structures are called quantum dots (0D), quantum wires (1D) or quantum wells (2D). The principal property of interest resides in their adjustable quantized energy spectrum. The corresponding wave functions are localized within the confined region, but may extend over many periods of its boundary crystal lattice. A quantum dot (QD) is therefore a giant artificial atom which enjoys prospects for an increasing range of future applications: *e.g.* as a semiconductor laser [1], as *qubits* for quantum information processing, as single-electron transistors in electronics, as artificial *fluorophores* for intra-operative detection of tumors, biological imaging or cell studies, *etc.*

QD properties depend on their electronic structure. In fact, they contain a finite number of elementary charge carriers (from a few to a hundred), which may be conduction band electrons, valence band holes or excitons of the host substrate. There exists a vast number of aspects related to their own interactions as well as with the ambient electromagnetic field. Correlation effects [2, 3], interactions with boundary electromagnetic modes [4], phonon interactions [5], magnetic field effects [6], just to cite only a few topics, are currently vigorously investigated.

In the early eighties, quantum size effects (QSE) occurred experimentally in spherical semiconductor QDs in the exploration of the optical properties of semiconductor microcrystals in an insulating matrix [7, 8]. This phenomena has been observed in a large range of other confined structures: *e.g.* in quantum ribbons or in quantum disks [9], in quantum wires [10] and, indeed, in quantum wells [11]. It emerges in a widening of the semiconductor optical band gap. This is due to the increase of confinement energy for decreasing QD size. The valence band drops and the conduction band rises. Both effects constitute the leading contribution to the characteristic blue-shift in the semiconductors optical spectra of such strongly quantum-confined systems [12, 13]. So, the confinement of oppositely charged carriers does have significant effects on the electron-hole Coulomb interaction and, therefore, on exciton formation.

In order to apprehend correctly the origin of these quantum size effects, a first theoretical attempt to describe electronic properties dependent semiconductor QDs has been elaborated upon a *particle-in-a-sphere* model in the effective-mass approximation (EMA) [12, 13, 14], in which both electron and hole behave as non-interacting electrons and holes, trapped in a spherical infinite potential well but with different masses. Since 1973, the QD spherical shape has been used [15] and continues to be very popular over the years [2, 12, 14, 16, 17]. Because of the usual assumption of parabolic band structure, their effective mass is commonly defined through the inverse of the second derivative of their kinetic energy with respect to their momentum. Except for a pioneering work [12], the Coulomb interaction between electron and hole has been included and the excitonic contribution to the ground state energy has been taking into account by the Ritz variational principle. Some other authors have developed their own EMA model based on finite potential wells and improved agreement with experimental data for a significant range of QD sizes [14, 18, 19]. We should also quote some other variational calculations, *e.g.* [20, 21, 22]. In addition to spherical clusters, the case of cylindrical shaped microcrystallites has been carefully treated and experimentally studied [18, 23, 24], as well as the case of quantum wires [25, 26]. Later on, more sophisticated models have been conceived. Some of them, called empirical tight-binding method (ETBM), have considered non-parabolic valence and/or conduction band(s) [27, 28]. Others have used a reformulation of the so-called $\mathbf{k}\cdot\mathbf{p}$ perturbation theory including non-parabolic bands [29, 30, 31] based upon the Baldereschi-Lipari Hamiltonian [15].

However, despite the existence of numerous theoretical and/or empirical models, to the best of our knowledge, there exists actually no simple and comprehensive one, which offers a significant analytical treatment of the problem. This is the reason why this paper propose an alternative single EMA model for spherical semiconductor microcrystals, which allows us to clarify some tricky points. Moreover, we are able to exhibit the existence of an effective potential, whose presence significantly changes the QD ground state at small QD radius. Furthermore, in this formalism, it finally becomes possible, as an achievement, to analytically calculate some important quantities, such as *e.g.* the function η introduced by Kayanuma in [14], with a good agreement with experimental results. To this end, we shall introduce our model and recall some general properties in Sec. **II**. Then, the two next Secs. **III** and **IV** are devoted to the analysis of the two limiting regimes of semiconductor QDs which we shall explicitely describe and in which we carry out analytic computations in some

details. Finally, in Sec. **V**, the new effective potential mentioned above is introduced and we show how it leads to improve numerical results, much closer to experimental data. In the concluding section, we summarize our main results and indicate possible future research perspectives.

II. QUANTUM DOT MODEL AND SOME GENERAL RESULTS

Since our aim is to understand the semiconductor optical bands blue-shift as a main effect, we shall discard spin effects (electron-hole spin coupling or external applied magnetic field) and consider non-relativistic spinless electron or hole, trapped in a confining infinite spherical potential well. There exist other models with parabolic confinement [3, 16] or parabolic potential superimposed to an infinite potential well [17], which are used to explain certain spectroscopic data; but the concept of a QD size is then not so well defined. Here, we adopt the EMA model previously introduced.

A. Intrinsic limitations

First, the EMA assumption breaks down when a significant number of carriers wave functions inside the QD overlap. Thus, our results are expected to fail for very small nanocrystals. As matter of fact, at typical sizes of less than a hundred lattice spacings appear, in a semiconductor, magic numbers of clusters of which only some remain stable: *e.g.* nanocrystalline silicon stay solely coherent as clusters of $Si_{12}, Si_{33}, Si_{39}$ and Si_{45}, if they contain less than 60 silicon atoms [32]. When such size is reached, their band structure should be very deformed and, therefore, cannot satisfy the parabolic spectrum assumption on which the EMA is based.

Second, by assuming spherical symmetry for the QD, we justify the splitting of the Schrödinger equation into a sum of a radial part and an angular part. This manipulation appreciably reduces the computation of the eigenstate wave functions and the energy eigenvalues. This approximation turns out often to be quite good since most synthesized nanocrystals possess an *aspect ratio* (defined as the ratio between the longest and shortest axes of the QD) smaller than 1.1. But, for high aspect ratio microcrystals, this spherical assumption becomes no longer valid.

Third, the real potential at the boundary of the QD is, of course, not infinite. Actually, there is a potential step with a standard height of magnitude from 1 to 3eV [21]. This value is generally quite large compared to typical electron and hole energies and, therefore, their tunnel conductivity from the nanocrystal to its surrounding should be neglected, except for very small QD sizes. Furthermore, the infinite potential well approximation implies that the charge carrier behavior inside a QD is totally insensitive to any externally applied potential or to the surrounding of the cluster. Although the surrounding effects may be sufficiently small to be neglected, the presence of a large external potential can in fact significantly modify the inside behavior of the microcrystallites. Thus, in order to test the validity of this approximation, we have to consider charged carriers isolated from the outside neighboring semiconductor.

B. A free Quantum Dot model

Let $V(r)$ be the confining potential well, defined in spherical coordinates as

$$V(\mathbf{r}) = V(r) = \begin{cases} 0 & \text{if } 0 \leq r \leq R, \quad \text{Region I;} \\ \infty & \text{if } \quad r > R, \qquad \text{Region II.} \end{cases}$$

Neglecting, for the moment, the electron-hole Coulomb interaction, in single parabolic band approximation, the Hamiltonian operator is (with $\hbar = 1$)

$$\begin{aligned} H_0 &= H_{\mathrm{e}} + H_{\mathrm{h}} + E_g \\ &= -\frac{\nabla_{\mathrm{e}}^2}{2m_{\mathrm{e}}^*} - \frac{\nabla_{\mathrm{h}}^2}{2m_{\mathrm{h}}^*} + V(\mathbf{r}_{\mathrm{e}}) + V(\mathbf{r}_{\mathrm{h}}) + E_{\mathrm{g}}, \end{aligned} \tag{1}$$

where $m_{\mathrm{e,h}}^*$ and $H_{\mathrm{e,h}}$ denote the effective mass and the confined Hamiltonian respectively of the electron and of the hole, and E_{g} is the semiconductor energy band gap. The semiconductor QD wave function can now be written as a product of its electronic and hole parts

$$\Psi(\mathbf{r}_{\mathrm{e}}, \mathbf{r}_{\mathrm{h}}) = \psi(\mathbf{r}_{\mathrm{e}})\psi(\mathbf{r}_{\mathrm{h}}).$$

The orthonormal eigenfunctions ψ_{lnm} are labelled by three quantum numbers: $l \in \mathbb{N}$, $n \in \mathbb{N}^* = \mathbb{N} - \{0\}$ and $m \in [\![-l, l]\!]$.

$$\begin{aligned} \psi_{lnm}(\mathbf{r}) &= \psi_{lnm}(r, \theta, \varphi) \\ &= \frac{\chi_{[0,R[}(r)}{R\mathrm{J}'_{\nu_l}(k_{ln})} \sqrt{\frac{2}{r}} \mathrm{J}_{\nu_l}\left(\frac{k_{ln}}{R} r\right) \mathrm{Y}_l^m(\theta, \varphi), \end{aligned}$$

where

- $\mathrm{Y}_l^m(\theta,\varphi)$ is the spherical harmonic of orbital quantum number l and azimuthal quantum number m,
- $\mathrm{J}_{\nu_l}(x)$ is the Bessel function of the first kind of index $\nu_l = l + \frac{1}{2}$ and variable x,
- $\chi_{[0,R[}(r)$ is the characteristic function of radial interval,
- $\{k_{ln}\}_{ln}$ are the wave numbers in Region I, defined as the n^{th} non-zero root of the Bessel function $\mathrm{J}_{\nu_l}(x)$, thanks to the continuity condition at $r = R$.

The respective energy eigenvalues for electron and hole are expressed in terms of the same family of wave numbers $\{k_{ln}\}_{ln}$

$$E_{ln}^{\mathrm{e,h}} = \frac{k_{ln}^2}{2m_{\mathrm{e,h}}^* R^2}.$$

This clearly indicates that the continuum density of states of the semiconductor bulk should show atomic-like discrete energy levels with increasing energy separation as the QD radius decreases.

C. Electron-hole pair Quantum Dot model

From now on, we add the Coulomb interaction V_{C} between electron and hole to the Hamiltonian H_0, given by Eq. (1) and define the usual spherical shape semiconductor QD Hamiltonian H in the effective-mass approximation [13, 14, 18, 19] as

$$\begin{aligned} H &= H_0 + V_{\mathrm{C}}(\mathbf{r}_{\mathrm{eh}}) \\ &= -\frac{\nabla_{\mathrm{e}}^2}{2m_{\mathrm{e}}^*} - \frac{\nabla_{\mathrm{h}}^2}{2m_{\mathrm{h}}^*} + V(\mathbf{r}_{\mathrm{e}}) + V(\mathbf{r}_{\mathrm{h}}) - \frac{e^2}{\kappa r_{\mathrm{eh}}} + E_{\mathrm{g}}, \end{aligned} \tag{2}$$

where $\kappa = 4\pi\varepsilon$ and ε is the semiconductor dielectric constant.

In order to simplify notations, we shall assume that $E_{\mathrm{g}} = 0$. Deriving an exact analytical solution is arduous because of the Coulomb potential dependence in the electron-hole relative distance $r_{\mathrm{eh}} = |\mathbf{r}_{\mathrm{eh}}| = |\mathbf{r}_{\mathrm{e}} - \mathbf{r}_{\mathrm{h}}|$, which explicitly breaks the spherical symmetry of the system. The common approach to this problem is to treat differently the interplay of the Coulomb interaction, which scales as $\propto R^{-1}$, and the quantum confinement, which scales as $\propto R^{-2}$. To handle these competing contributions, two regimes of electron-hole pair should be singled

out by comparing the order of magnitude of the QD radius R to the Bohr radius of the bulk MOTT-WANNIER exciton $a^* = \dfrac{\kappa}{e^2\mu}$, μ being the reduced mass of the exciton. These are

- the strong confinement regime, valid for a size $R \leq 2a^*$ [14], in which the potential well strongly affects the relative electron-hole motion, the *exciton* states consist then of uncorrelated electron and hole states;

- the weak confinement regime, valid for a size $R \geq 4a^*$ [14], in which the electron-hole relative motion and its binding energy are *quasi* left unchanged. The exciton could be treated as a confined quasi-particle of total mass $M = m_{\rm e}^* + m_{\rm h}^*$ and its center-of-mass motion should be quantized.

In any case, the Coulomb potential should be treated as a perturbation of the infinite confinement potential well. So, in order to evaluate the ground state energy of the exciton state using a variational procedure, we shall use the following wave function

$$\phi(\mathbf{r}_{\rm e}, \mathbf{r}_{\rm h}) = \psi_{010}(\mathbf{r}_{\rm e})\psi_{010}(\mathbf{r}_{\rm h})\phi_{\rm rel}(\mathbf{r}_{\rm eh}), \tag{3}$$

where $\phi_{\rm rel}(\mathbf{r}_{\rm eh}) = \phi_{\rm rel}(r_{\rm eh}) = {\rm e}^{-\frac{\sigma}{2}r_{\rm eh}}$, σ denotes a variational parameter, $r_{\rm e,h} = |\mathbf{r}_{\rm e,h}|$, and

$$\psi_{010}(\mathbf{r}_{\rm e,h}) = \psi_{010}(r_{\rm e,h}) = -\frac{\chi_{[0,R]}(r_{\rm e,h})}{r_{\rm e,h}\sqrt{2\pi R}}\sin\Big(\frac{\pi}{R}r_{\rm e,h}\Big).$$

The variational wave function (3) is the most natural choice we can make. The wave function $\psi_{010}(\mathbf{r}_{\rm e})\psi_{010}(\mathbf{r}_{\rm h})$ is simply the *free* Hamiltonian H_0 ground state. Its presence in the trial function $\phi(\mathbf{r}_{\rm e}, \mathbf{r}_{\rm h})$ insures the validity of the perturbation result to which the variational principle leads. Furthermore, in relative coordinates, the perturbation function $\phi_{\rm rel}(r_{\rm eh})$ exhibits the exciton behavior, which is that of a hydrogen-like atom with a charge carrier mass μ. Because of this analogy, we expect the variational parameter σ to depend on the Bohr radius as $\sigma \propto a^{*-1}$. Notably, in the weak confinement regime, the exciton ground state, which is a bound state, should mean that $\sigma \approx 2a^{*-1}$, so that $\phi_{\rm rel}(r_{\rm eh}) = {\rm e}^{-\frac{r_{\rm eh}}{a^*}}$ — which is, up to a normalization constant, the ground state wave function of an hydrogen-like atom with its appropriate Bohr radius.

Let us make a trivial remark which will be the basic argument for our later purpose: the spherical shape of the QD explicitly breaks the translation invariance of the Coulomb interaction. This remark on translation invariance and spherical symmetry breakdown, as a whole, suggests the use of a Fourier transform formalism in relative coordinates. Let $\mathcal{F}[f]$

stands for the Fourier transform of the function f. Therefore, important matrix elements, such as the square of the variational wave function norm, the diagonal matrix element of the Coulomb electron-hole potential and the mean value of the electron-hole *free* Hamiltonian H_0 in this variational state, may be advantageously computed with Fourier transforms of functions.

The square of the norm of ϕ is then given by

$$\begin{aligned}
&\langle\phi|\phi\rangle \\
&= \int \mathrm{d}^3\mathbf{r}_\mathrm{e}\mathrm{d}^3\mathbf{r}_\mathrm{h}\psi_{010}^2(\mathbf{r}_\mathrm{e})\psi_{010}^2(\mathbf{r}_\mathrm{h})\phi_\mathrm{rel}^2(\mathbf{r}_\mathrm{eh}) \\
&= \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\mathcal{F}\big[\phi_\mathrm{rel}^2\big](\mathbf{k})\mathcal{F}\big[\psi_{010}^2\big](\mathbf{k})^2 \\
&= \frac{-8}{R^2}\partial_\sigma\frac{1}{\sigma}\iint_\mathcal{D}\frac{\mathrm{d}x}{x}\frac{\mathrm{d}y}{y}\sin^2(\pi x)\sin^2(\pi y)\sinh(\sigma R x)\mathrm{e}^{-\sigma R y},
\end{aligned} \tag{4}$$

where $\mathcal{D} = \{(x,y) \in \mathbb{R}^2 / 0 \leq x \leq y \leq 1\}$, while the different Fourier transforms are

$$\begin{cases}
\mathcal{F}\big[\phi_\mathrm{rel}^2\big](\mathbf{k}) = -4\pi\partial_\sigma\dfrac{1}{\sigma^2+k^2}, \\
\mathcal{F}\big[\psi_{010}^2\big](\mathbf{k}) = \dfrac{2}{kR}\displaystyle\int_0^1\frac{\mathrm{d}x}{x}\sin^2(\pi x)\sin(kRx).
\end{cases}$$

Moreover, the diagonal matrix element of the electron-hole Coulomb potential is

$$\begin{aligned}
&\langle\phi|V_\mathrm{C}(r_\mathrm{eh})|\phi\rangle \\
&= -\frac{e^2}{\kappa}\int\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\mathcal{F}[\varphi_\mathrm{rel}](\mathbf{k})\mathcal{F}\big[\psi_{010}^2\big](\mathbf{k})^2 \\
&= \frac{-e^2}{\kappa R}\frac{8}{\sigma}\iint_\mathcal{D}\frac{\mathrm{d}x}{x}\frac{\mathrm{d}y}{y}\sin^2(\pi x)\sin^2(\pi y)\sinh(\sigma R x)\mathrm{e}^{-\sigma R y},
\end{aligned} \tag{5}$$

with $\varphi_\mathrm{rel}(\mathbf{r}_\mathrm{eh}) = \dfrac{|\phi_\mathrm{rel}(r_\mathrm{eh})|^2}{r_\mathrm{eh}}$. Lastly, the mean value of the electron-hole Hamiltonian H_0 can be exactly evaluated as

$$\frac{\langle\phi|H_0|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\pi^2}{2\mu R^2} + \frac{\sigma^2}{8\mu} = \frac{\pi^2}{2\mu R^2} + \frac{E^*}{4}\sigma'^2, \tag{6}$$

where the dimensionless variational parameter σ' is defined by $\sigma = \dfrac{\sigma'}{a^*}$ and the exciton Rydberg energy by $E^* = \dfrac{1}{2\mu a^{*2}}$.

As Eqs. (3), (4), (5) and (6) are obtained without any further approximations — except the ones upon which the model was built —, they have to be valid everywhere whether it is, by construction, in the strong confinement regime or, by extension, in the weak confinement regime. Indeed, the Coulomb interaction itself should be always treated as a perturbation with respect to the infinite potential well, although its energetic contribution should not be maintained as a perturbation to the exciton confinement energy. Thus, the trial function global form (3) will remain acceptable in the weak confinement regime, but we will have to correct it by adding a further phase factor, which will depends only on the center-of-mass coordinates.

We now study the behavior of these quantities and describe some of their consequences in different ranges of QD radii for which $\sigma R \ll 1$ or $\sigma R \gg 1$, (corresponding respectively to the strong and the weak confinement regimes) and for which we can analytically and explicitly compute numerical values.

III. STRONG CONFINEMENT REGIME

In this regime, where $\sigma R \ll 1$, the assumed form of the variational wave function (3) shall be used and it is appropriate to perform Taylor expansions in Eqs. (4) and (5) in the neighborhood of the dimensionless parameter $\sigma R = 0$. Because of the analyticity of the Taylor expansion of the functions $\exp(x)$ and $\sinh(x)$, this expansion will remain valid up to $\sigma R \lesssim 1$. Thus, we obtain

$$\begin{cases} \langle\phi|V_{\mathrm{C}}(r_{\mathrm{eh}})|\phi\rangle = -\dfrac{\mathrm{e}^2}{\kappa R}\left\{A - \sigma R + \dfrac{B}{2}\sigma^2 R^2 + \mathcal{O}(\sigma^3 R^3)\right\}, \\ \langle\phi|\phi\rangle = 1 - B\sigma R + C\sigma^2 R^2 + \mathcal{O}(\sigma^3 R^3), \end{cases} \tag{7}$$

where the constants A, B and C are given in closed form by

$$\begin{aligned} A &= 2 - \frac{2\mathrm{Si}(2\pi) - \mathrm{Si}(4\pi)}{2\pi} \approx 1.786, \\ B &= \frac{2}{3}\left\{\frac{10}{9} - \frac{2}{3\pi^2} + \frac{2\mathrm{Si}(2\pi) - \mathrm{Si}(4\pi)}{8\pi^3}\right\} \approx 0.699, \\ C &= \frac{1}{3} - \frac{1}{2\pi^2} \approx 0.283. \end{aligned}$$

Here, $\mathrm{Si}(x)$ denotes the sine integral

$$\mathrm{Si}(x) = \int_0^x \frac{\mathrm{d}t}{t}\sin(t), \ \forall x \in \mathbb{R}.$$

Consequently, we can deduce an expression of the mean value of the total Hamiltonian H in the strong confinement regime as an expansion in powers of σ', which is the dimensionless variational parameter first introduced in Eq. (6)

$$\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\pi^2}{2\mu R^2} - A\frac{e^2}{\kappa R} - 2(AB-1)E^*\sigma' + \frac{E^*}{4}\sigma'^2 + \dots$$

where the correction terms "..." go to zero at least as fast as $\propto \frac{R}{a^*}$. The variational parameter σ' is now determined by minimizing the expectation value of the energy. Thus, we find $\sigma'_0 = 4(AB-1) \approx 0.996$ and the corresponding energy value is

$$\begin{aligned} E_{\rm eh}^{\rm strong} &= \frac{\pi^2}{2\mu R^2} - A\frac{e^2}{\kappa R} - 4(AB-1)^2 E^* \\ &\approx \frac{\pi^2}{2\mu R^2} - 1.786\frac{e^2}{\kappa R} - 0.248E^*. \end{aligned} \tag{8}$$

In the strong confinement regime, this formula has been already analytically obtained [14, 33] with trial functions showing the same global form as the previously presented one (3) but with an interactive part chosen, instead of $\phi_{\rm rel}(\mathbf{r}_{\rm eh})$, equal to

$$\widetilde{\phi}_{\rm rel}(\mathbf{r}_{\rm eh}) = 1 - \frac{\sigma}{2} r_{\rm eh}.$$

This choice corresponds in fact to the two first terms of the Taylor expansion of Eq. (3) in the neighborhood of $\frac{\sigma}{2} r_{\rm eh} \leq \sigma R \ll 1$. In the meantime, we have succeeded in finding an approximate value of its upper bound for $R \lesssim a^*$. This bound, as we already mentioned in Subsec. **II C**, can be in turn numerically extend to the commonly accepted region of validity of QD radii, *i.e.* $R \lesssim 2a^*$.

IV. WEAK CONFINEMENT REGIME

As previously explained, in this regime $\sigma R \gg 1$, we can retain the global form of the trial function used in the strong confinement regime because of the presence of the confinement potential. But, as said before, the physical situation requires a modification, before applying the variational procedure.

A. Considerations on the trial function

Here, the electron-hole pair states consist in binding exciton states, which globally act like quasi-particles of total mass M. As matter of fact, in a translation invariant space region,

the quasi-particle point of view emphasizes the possibility for the exciton to show a global translational motion in terms of its center-of-mass coordinates. In the weak confinement regime, the exciton typical size $\propto a^*$ is sufficiently smaller than the QD typical radius R. So, we can reasonably assume that excitons should exhibit a quasi-particle behavior and possess a global translational motion. In order to account for a partial restoration of translation invariance, in the weak confinement regime, we have to introduce a center-of-mass coordinates plane wave, because the physical behavior of the confined exciton should show a reminiscence of the free exciton one, *i.e.* the wave function of the ground state of the exciton shall be considered as the wave function of quasi-particle describing the electron-hole pair. Thus, it should have the form

$$\psi(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h}) = \psi_{010}(\mathbf{r}_\mathrm{e})\psi_{010}(\mathbf{r}_\mathrm{h})\phi_\mathrm{rel}(\mathbf{r}_\mathrm{eh})\phi_\mathrm{e}(\mathbf{r}_\mathrm{e})\phi_\mathrm{h}(\mathbf{r}_\mathrm{h}), \tag{9}$$

where $\phi_\mathrm{e,h}(\mathbf{r}_\mathrm{e,h}) = \mathrm{e}^{i\frac{\pi}{R}\boldsymbol{\sigma}_\mathrm{e,h}\cdot\mathbf{r}_\mathrm{e,h}}$. The vectors $\boldsymbol{\sigma}_\mathrm{e,h}$ are dimensionless quantities which facilitate the computation in practice but are not directly physically interpretable. In fact, in order to understand properly the meaning of these parameters, we have to define the wave numbers vectors respectively in the center-of-mass and in the relative coordinates as

$$\begin{cases} \boldsymbol{\sigma}_\mathrm{G} = \boldsymbol{\sigma}_\mathrm{e} + \boldsymbol{\sigma}_\mathrm{h}, \\ \boldsymbol{\sigma}_\mathrm{eh} = \dfrac{m_\mathrm{h}^*\boldsymbol{\sigma}_\mathrm{e} - m_\mathrm{e}^*\boldsymbol{\sigma}_h}{M}. \end{cases}$$

Since $\boldsymbol{\sigma}_\mathrm{e}\cdot\mathbf{r}_\mathrm{e} + \boldsymbol{\sigma}_\mathrm{h}\cdot\mathbf{r}_\mathrm{h} = \boldsymbol{\sigma}_\mathrm{G}\cdot\mathbf{r}_\mathrm{G} + \boldsymbol{\sigma}_\mathrm{eh}\cdot\mathbf{r}_\mathrm{eh}$, the functions $\phi_\mathrm{e,h}(\mathbf{r}_\mathrm{e,h})$ should contribute to the exciton total energy by an additional kinetic term, corresponding to the fundamental energy of a plane wave in a space region of size R in the center-of-mass coordinates $\mathbf{r}_\mathrm{G}$, $\propto \dfrac{|\boldsymbol{\sigma}_\mathrm{e}|^2}{m_\mathrm{e}^*} + \dfrac{|\boldsymbol{\sigma}_\mathrm{h}|^2}{m_\mathrm{h}^*} = \dfrac{|\boldsymbol{\sigma}_\mathrm{G}|^2}{M} + \dfrac{|\boldsymbol{\sigma}_\mathrm{eh}|^2}{\mu}$, which is assumed to be of the form $\dfrac{\pi^2}{2MR^2}$. This constraint is consistent with the conditions

$$\begin{cases} |\boldsymbol{\sigma}_\mathrm{G}|^2 = 1 \\ \boldsymbol{\sigma}_\mathrm{eh} = \mathbf{0} \end{cases} \Longrightarrow \begin{cases} |\boldsymbol{\sigma}_\mathrm{e}|^2 = \dfrac{1}{(1+\lambda)^2} \\ |\boldsymbol{\sigma}_\mathrm{h}|^2 = \dfrac{\lambda^2}{(1+\lambda)^2} \end{cases}$$

where $\lambda = \dfrac{m_\mathrm{h}^*}{m_\mathrm{e}^*}$. The previous expressions reinforce the cogency of the trial wave function $\psi(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h})$. Taking $\boldsymbol{\sigma}_\mathrm{eh} = \mathbf{0}$ does not provide an extra kinetic energy term to the total exciton energy in the relative coordinates, except the ones due to the electron and hole confinement. But taking $|\boldsymbol{\sigma}_\mathrm{G}|^2 = 1$ adds to the electron-hole pair total energy the correct energetic contribution in the center-of-mass coordinates, corresponding to the fundamental energy of a confined particle of mass M.

B. Variational principle

The trial function (9) leaves unchanged the exciton density of probability or the Coulomb potential matrix element

$$\langle\psi|\psi\rangle = \langle\phi|\phi\rangle \;\text{ and }\; \langle\psi|V_{\rm C}(r_{\rm eh})|\psi\rangle = \langle\phi|V_{\rm C}(r_{\rm eh})|\phi\rangle,$$

whereas the free Hamiltonian matrix element gets further contributions, *i.e.*

$$\begin{aligned}\frac{\langle\psi|H_0|\psi\rangle}{\langle\psi|\psi\rangle} &= \frac{\pi^2}{2\mu R^2} + \frac{\pi^2}{2R^2}\left\{\frac{|\boldsymbol{\sigma}_{\rm e}|^2}{m_{\rm e}^*} + \frac{|\boldsymbol{\sigma}_{\rm h}|^2}{m_{\rm h}^*}\right\} + \frac{E^*}{4}\sigma'^2 \\ &= \frac{\pi^2}{2\mu R^2} + \frac{\pi^2}{2MR^2} + \frac{E^*}{4}\sigma'^2.\end{aligned}$$

In order to evaluate the mean value of the Coulomb potential in the quantum state defined by the wave function ψ, we have to compute the following double integral in the weak confinement regime for $\sigma R \gtrsim 2\pi$. Since for such QD radii, the convergence of all occurring series is insured, we can write

$$\begin{aligned}&\iint_{\mathcal{D}} \frac{{\rm d}x}{x}\frac{{\rm d}y}{y}\sin^2(\pi x)\sin^2(\pi y)\sinh(\sigma R x){\rm e}^{-\sigma R y} \\ &= \iint_{0\le x\le y\le \sigma R} \frac{{\rm d}x}{x}\frac{{\rm d}y}{y}\sin^2\Big(\frac{\pi}{\sigma R}x\Big)\sin^2\Big(\frac{\pi}{\sigma R}y\Big)\sinh(x){\rm e}^{-y} \\ &= \frac{\pi^2}{2\sigma^2R^2}\sum_{k\ge 0}\frac{1}{k+1}\left(-\frac{4\pi^2}{\sigma^2R^2}\right)^k\int_0^{\sigma R}\frac{{\rm d}y}{y}\sin^2\Big(\frac{\pi}{\sigma R}y\Big)\left\{{\rm e}^{-2y}\sum_{n=0}^{2k+1}\frac{y^n}{n!} - \sum_{n=0}^{2k+1}\frac{(-y)^n}{n!}\right\} \\ &= \frac{2\pi^2}{\sigma R}\sum_{n\ge 0}\frac{(-4\pi^2)^n}{(2(n+1))!}\,{}_2{\rm F}_1\left(n+1,1;n+2;-\frac{4\pi^2}{\sigma^2R^2}\right) \\ &\qquad\times\left\{\int_0^1\frac{{\rm d}y}{y}\sin^2(\pi y)y^{2n+1}\cosh(\sigma R y) - \frac{2n+1}{\sigma R}\int_0^1{\rm d}y\,y^{2n}\sinh(\sigma R y)\right\},\end{aligned} \tag{10}$$

where ${}_2{\rm F}_1(a,b;c;z) = \displaystyle\sum_{n\ge 0}\frac{(a)_n(b)_n}{(c)_n}\frac{z^n}{n!}$ is the usual Gauss hypergeometric function. In Eq. (10), we take terms up to the fourth order in the variable $\dfrac{\pi}{\sigma R}$ in the neighborhood of 0. Therefore, for the terms in Eq. (10) whose integrand is not exponentially decreasing for $y \to \sigma R \gg 1$, we get

$$\begin{aligned}&-\frac{\pi^2}{2\sigma R}\int_0^{\sigma R}\frac{{\rm d}y}{y}\sin^2\Big(\frac{\pi}{\sigma R}y\Big)\sum_{k\ge 0}\frac{1}{k+1}\left(-\frac{4\pi^2}{\sigma^2R^2}\right)^k\sum_{n=0}^{2k+1}\frac{(-y)^n}{n!} \\ &= A' - \frac{B'}{\sigma R} + C'\frac{\pi^2}{\sigma^2R^2} - D'\frac{\pi^3}{\sigma^3R^3} + E'\frac{\pi^4}{\sigma^4R^4} + \mathcal{O}\left(\frac{\pi^5}{\sigma^5R^5}\right);\end{aligned} \tag{11}$$

with

$$A' = \frac{\pi}{2}\left\{\mathrm{Si}(2\pi) - \frac{\mathrm{Si}(4\pi)}{2}\right\} \approx 1.056,\ B' = 0,$$
$$C' = -\frac{4}{3}A',\ D' = \frac{\pi}{4}\ \text{ and }\ E' = \frac{4}{5}\left(A' - \frac{1}{8}\right).$$

Furthermore, for terms in Eq. (10) whose integrand is exponentially decreasing for $y \to \sigma R \gg 1$, we apply Laplace method (*cf.* Appendix **A**) to get an answer in the limit of $\sigma R \to \infty$. Hence,

$$\pi^2 \sum_{n\geq 0} \frac{(-4\pi^2)^n}{(2(n+1))!}\, {}_2\mathrm{F}_1\left(n+1, 1; n+2; -\frac{4\pi^2}{\sigma^2 R^2}\right) \int_0^1 \frac{\mathrm{d}y}{y} \mathrm{e}^{-2\sigma R y} \sin^2(\pi y) \left\{ y^{2n+1} + \frac{2n+1}{\sigma R} y^{2n} \right\}$$
$$= \frac{\pi^3}{\sigma^3 R^3}\left\{\frac{\pi}{4} + \mathcal{O}\left(\frac{\pi^2}{\sigma^2 R^2}\right)\right\}. \tag{12}$$

In the QD radii range, where the third order actually contributes to Eq. (11), *i.e.* for radii near the lower bound of the possible radii in the weak confinement regime $\sigma R \approx 2\pi$ — which, as we will see later, corresponds to a size $R \approx \pi a^*$ —, the third and fourth order terms contribute to the exciton energy with terms of the same order of magnitude. But for radii larger than $4a^*$ [14], the third and also the fourth order terms are in fact irrelevant. So, we can stop the expansion in Eq. (11) at the second order term. Thus, the Coulomb interaction diagonal matrix element and the square of the norm become

$$\begin{cases} \langle\psi|V_{\mathrm{C}}(r_{\mathrm{eh}})|\psi\rangle = -\dfrac{e^2}{\kappa R}\dfrac{8A'}{\sigma^2 R^2}\left\{1 - \dfrac{4}{3}\dfrac{\pi^2}{\sigma^2 R^2} + \dfrac{D''}{A'}\dfrac{\pi^3}{\sigma^3 R^3} + \mathcal{O}\left(\dfrac{\pi^4}{\sigma^4 R^4}\right)\right\}, \\ \langle\psi|\psi\rangle = \dfrac{16A'}{\sigma^3 R^3}\left\{1 - \dfrac{8}{3}\dfrac{\pi^2}{\sigma^2 R^2} + \dfrac{5}{2}\dfrac{D''}{A'}\dfrac{\pi^3}{\sigma^3 R^3} + \mathcal{O}\left(\dfrac{\pi^4}{\sigma^4 R^4}\right)\right\}, \end{cases} \tag{13}$$

where by definition $D'' = \dfrac{E'}{2} \approx 0.372$. Finally, we obtain in this regime the following σ'-expansion of the variational energy

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\pi^2}{2\mu R^2} + \frac{\pi^2}{2MR^2} + \frac{E^*}{4}\sigma'^2 - E^*\sigma' - \frac{2}{3}\frac{\pi^2}{\mu R^2}\frac{1}{\sigma'} + \frac{3}{4}\frac{D''}{A'}\pi\frac{\pi^2}{\mu R^2}\frac{1}{\sigma'^2}\frac{a^*}{R} + \ldots$$

Applying now the variational principle, we get the value of the dimensionless variational parameter σ'

$$\sigma'_0 = 2 - \frac{2}{3}\pi^2\left(\frac{a^*}{R}\right)^2 + \frac{3}{4}\frac{D''}{A'}\pi^3\left(\frac{a^*}{R}\right)^3.$$

Because the second and the third terms in the previous expression do not contribute to the total electron-hole pair energy, we conclude that $\sigma_0' \approx 2$ and

$$\begin{aligned} E_{\mathrm{eh}}^{\mathrm{weak}} &= -E^* + \frac{\pi^2}{6\mu R^2} + \frac{\pi^2}{2MR^2} + \delta\frac{\pi^2}{\mu R^2}\frac{a^*}{R} \\ &= -E^* + \frac{\pi^2}{6\mu R^2} + \frac{\pi^2}{2M(R-\eta(\lambda)a^*)^2}, \end{aligned} \tag{14}$$

from which we are able to extract an explicit expression for the Kayanuma-function as $\eta(\lambda) = \delta\dfrac{(1+\lambda)^2}{\lambda}$ with $\delta = \dfrac{3}{16}\dfrac{D''}{A'}\pi = \dfrac{3\pi}{40}\left(1 - \dfrac{1}{8A'}\right) \approx 0.208$ and $\lambda = \dfrac{m_{\mathrm{h}}^*}{m_{\mathrm{e}}^*}$. As we have already specified, let us observe that $\sigma_0' \approx 2$ implies that $R \gtrsim \pi a^*$, which is *surprisingly* consistent with the usually accepted numerical region of validity. Moreover, we see that the interaction part $\phi_{\mathrm{rel}}(\mathbf{r}_{\mathrm{eh}})$ of the wave function coincides with the ground state wave function of a reduced mass μ hydrogen-like atom up to a normalization factor and contributes to the excitonic total energy with the leading binding fundamental energetic term $-E^*$, as we expect.

The η-function was first introduced phenomenologically by Eq. (28) in [14] to get a better fit between numerical and empirical results; but no analytic derivation of it is available so far. First, here, we manage to give an expression for this function, which satisfies the electron-hole exchange symmetry: $\lambda \longrightarrow \lambda^{-1}$. Second, as was already depicted by Kayanuma, the QD size *renormalization* term $\eta(\lambda)a^*$ is interpretable as the so-called dead layer [34]: this is the physical reminiscence of the fact that, although it could be successfully described as a quasi-particle, the exciton is not actually itself an indivisible particle. In fact, its center-of-mass motion, the one on which the quantization is really performed, could not reach the infinite potential well surface unless the exciton undergoes a strong deformation in the relative motion of the electron and the hole. This implies that the picture of a point-like exciton is no longer appropriate in this region of space. The most convenient way to study this exciton consists in thinking of it as a rigid sphere of radius $\propto a^*$, where the proportional factor must not exceed $\frac{3}{2}$ too much, because $l^* = \frac{3}{2}a^*$ is the mean value of the relative distance between the electron and the hole in the non-confined exciton ground state. We have to get the largest possible radius l^* for the sphere picture, when $\lambda \to \infty$, *i.e.* in the limit of infinite hole mass because the hole stays motionless at the center-of-mass of the electron-hole system. Furthermore, the smallest possible radius must be obtained in the symmetrical case $\lambda = 1$ and must be held at $\frac{1}{2}l^* = \frac{3}{4}a^*$, which imposes $\eta(1) \approx 0.75$. This matches quite well with both experimental and theoretical results as shown in Tab. I.

Finally, regarding the different values of $\eta(\lambda)$ around $\frac{3}{2}$ at $\lambda = 5$, we can safely conclude that the picture of infinite hole mass becomes valid as soon as $\lambda \approx 5$.

Table I: Comparison between numerical and analytical values for the η-function.

λ	1	3	5
$\eta_{\mathrm{num}}(\lambda)$	0.73	1.1	1.4
$\eta_{\mathrm{theo}}(\lambda)$	0.83	1.1	1.5
relative error	14%	<1%	7%

In Tab. I, we compare numerical values computed from numerical simulations taken by this function $\eta(\lambda)$ for $\lambda = 1, 3, 5$ to those theoretically predicted by the previous relation and note that there exists a reasonable agreement between both results. We even succeed to enlarge the region, in which the weak confinement regime is satisfactory.

V. A PSEUDO-POTENTIAL-LIKE METHOD

The problem, that we still have to deal with, consists in finding a physical way to substract off the term reminiscent of the kinetic energy term in Eq. (14). As matter of fact, because of the presence of the reduced mass, it is interpretable as a kinetic energy term in the relative coordinates. However, this type of exciton kinetic energy has to be already contained in the Rydberg energy term, because of the validity of the Virial theorem in the relative coordinates. Besides, in this assumption, the higher order contributions to the electron-hole energy must be interpreted as higher order contributions to the kinetic energy of the exciton, viewed as a quasi-particle of mass M, which physically justifies the intuitive idea that for very large radius R only the quasi-particle point of view should be responsible for the exciton kinetic energy.

A. Weak confinement regime

In analogy with the pseudo-potential method for metals, we propose to introduce an additional potential term W in the Hamiltonian H, which shall depend only on the electron-

hole relative distance $r_{\rm eh}$, so that it contributes to the second order of the exciton total energy but not to the third order — *i.e.* the one which allows us to determine the expectation value of the η-function. Furthermore, we assume that W must

- be attractive at distances in the range of a^* in order to promote excitonic state with typical size around his Bohr radius;
- be repulsive at short distances in order to penalize excitonic state with small size and to remind that the exciton typical size should not be smaller that the typical size of the surrounding lattice spacing;
- be exponentially small for large distances, in order to not perturb the long range Coulomb interaction.

Consequently a natural choice of such potential should be of the form

$$W(\mathbf{r}_{\rm eh}) = -\frac{32\pi^2}{9} E^* \frac{r_{\rm eh}^2}{R^2} {\rm e}^{-2\frac{r_{\rm eh}}{a^*}}. \tag{15}$$

Inspection shows that it satisfies all of the previous constraints; and, in the weak confinement regime, it exactly provides us what we ask for

$$\frac{\langle\psi|W(\mathbf{r}_{\rm eh})|\psi\rangle}{\langle\psi|\psi\rangle} = -\frac{\pi^2}{6\mu R^2}\left\{1 + \mathcal{O}\left(\frac{a^{*2}}{R^2}\right)\right\}.$$

Remark. The potential amplitude in Eq. (15) is fixed *ad hoc* in order to get the previous correct kinetic energy contribution. Consequently, the pseudo-potential form we choose seems to be arbitrary. However, the form of $W(r_{\rm eh}) \propto r_{\rm eh}^2 {\rm e}^{-2\frac{r_{\rm eh}}{a^*}}$ is the only one which straightforwardly first contributes to the second order term in both weak and strong confinement regimes and which does not change the exciton energy behavior to zeroth and first order terms.

B. Strong confinement regime

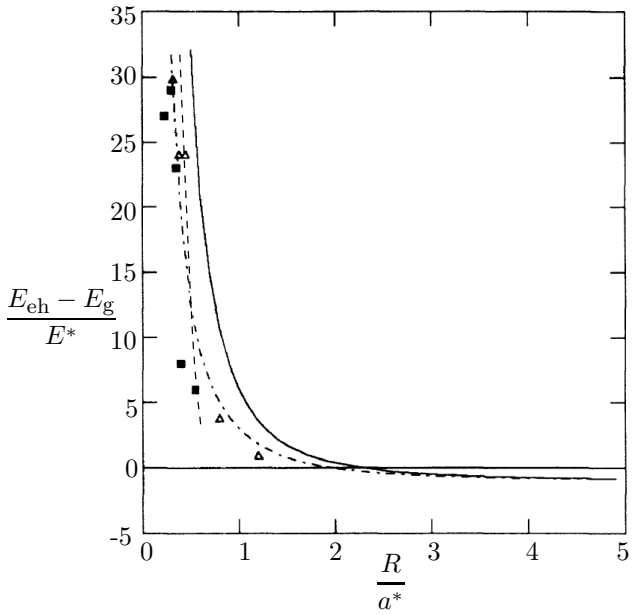
As we have introduced a new term in the exciton total Hamiltonian H, we have to check its consequences in the strong confinement regime. The most important one is the significant decrease of the expected value of the exciton energy because of the exciton total Hamiltonian

redefinition: $H' = H + W$. In fact, the pseudo-potential W contributes to the second order as

$$\frac{\langle\phi|W(\mathbf{r}_{\rm eh})|\phi\rangle}{\langle\phi|\phi\rangle} = -\frac{64\pi^2}{9}CE^*\left\{1+\mathcal{O}\left(\frac{R}{a^*}\right)\right\} \approx -19.9E^* + \ldots$$

This expression is deduced by a reasoning similar to that of Sec. **III**. Therefore, we must keep in mind that it is only valid when $2R \lesssim a^*$ because of the pseudo-potential exponential dependence, which changes the validity conditions of the Taylor expansion we made.

Figure 1: Behavior of the excitonic ground state energy as a function of the QD radius computed for a confining infinite potential well with (−−) or without (—) the presence of the pseudo-potential W and for a confining finite potential step of height $V_0 \approx 1$eV (−·−) [21] and compared to experimental results for CdS [35] microcrystallites with material parameters: $\varepsilon = 11.6$, $m_{\rm e}^* = 0.235m_{\rm e}$, $m_{\rm h}^* = 1.35m_{\rm e}$, $E_{\rm g} = 2.583$eV, $E^* = 27$meV and $a^* = 30.1$Å, where $m_{\rm e}$ is the electron bare mass.



As we can see from Fig. 1, the excitonic energy computed in the presence of the pseudo-potential gets a *significant* better fit to experimental results, in the validity domain $2R \lesssim a^*$, than the one calculated without this tool. Nevertheless, the divergence for very small QD size still holds as a consequence of the infinite potential well assumption. In order to extend the validity domain upper bound, it would be efficient to carry on the energy expansion

to one or maybe to two further orders. But, at this point, the computation become quite involved and we cannot insure the success or even the relevance of this approach.

VI. CONCLUSION

By using an improved EMA model, we are able to obtain well known results in the strong confinement regime, to correctly apprehend the weak confinement regime by adding a pseudo-potential term to the total Hamiltonian describing the electron-hole dynamics and to find an nice analytical expression for the phenomenological function η of Kayanuma.

As we have shown, the introduction of the pseudo-potential W allows to reduce in part the overestimation due to the infinite potential well observed in [21], particularly near the upper boundary $2R \approx a^*$, even if it still does not accurately approximate the total energy for much smaller QDs. For such QD sizes, the best approach would probably require a finite confinement potential. Thus, a future research work might focus on applying this pseudo-potential method, in the presence of a confining finite potential step, in order to obtain a hopefully better behavior for excitons in very small QDs.

Appendix A: THE LAPLACE METHOD

The purpose of this method is to study asymptotic behavior of integrals like $I(t) = \int_0^a \mathrm{d}x\, g(x)\mathrm{e}^{th(x)}$ and rigorously determine a mathematical equivalent for such quantities when $t \to \infty$.

One can prove the following theorem [36]: Let $a > 0$ and $g, h : [0, a] \longrightarrow \mathbb{R}$ two continuous mappings such that

i. $\int_0^a \mathrm{d}x\, |g(x)|\mathrm{e}^{h(x)} < \infty$;

ii. $\exists \delta_0 > 0 \ / \ \forall \delta \in [0, \delta_0]$ and $\forall x \in [\delta, a[,\ h(x) \leq h(\delta)$;

iii. $g(x) \underset{x0^+}{\sim} Ax^\alpha$ and $h(x) = b - cx^\beta + o(x^\beta)$, where $\alpha > -1$ and $c, \beta > 0$.

Then, $I(t) \underset{t\infty}{\sim} \frac{A}{\beta}\Gamma\left(\frac{\alpha+1}{\beta}\right)\mathrm{e}^{bt}(ct)^{-\frac{\alpha+1}{\beta}}$.

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